Peter, Robert

3978

LOWER BLUE LICK SPRING.

The quantitative chemical analysis of the water of the Lower Blue Lick Spring, in Nicholas county, Ky; with remarks on some other Salt Springs of the Blue Limestone formation.

BY ROBERT PETER, M. D.,

Prof. of Medical Chemistry, &c., in the Kentucky School of Medicine, and in Transylvania University.

Although this celebrated water has, at various times, been *qualitatively tested*, and the nature of its principal larger ingredients ascertained,* yet it has never been fully analyzed *quantitatively*, and the presence and proportions of its minuter constituents made out. To ascertain the exact weights and proportions of these several ingredients, and to detect and estimate the more minute, yet not less valuable medicinal agents of this water, was the object of the new investigation.

Nor is this object devoid of interest to the physician or the man of science. Chemical analysis frequently owe all their value to the minute ingredients which are detected. For example; the analysis of a soil is of very minor importance when it does not develope the proportions of the potash or phosphate of lime, and mineral waters frequently present medicinal virtues, in their use, which cannot be accounted for in the properties of the ingredients which are shown by a rough and imperfect analysis. Thus, the salt-sulphur water of Leamington, England, possesses virtues in the cure of scrofula, &c., which were unaccountable to physicians until by the minute analysis of Prof. Daubeny, iodine and bromine were detected in it in small quantities.

The water of the Lower Blue Lick Springs, has an extensive reputation in Kentucky and in the South generally; this being one of the oldest and best known watering places in the valley of the Ohio and Mississippi. Hundreds of invalids, as well as of seekers for recreation and pleasure, visit this pleasant locality every season,† and thousands of barrels and of bottles of the water are annually put up for distant places in this and other States‡

This remarkable spring, it is well known, attracted the attention of the earliest settlers of Kentucky, by its strong odor of sulphuretted hydrogen and the saltness of its waters. It was, indeed, from this source that Boone and other pioneers obtained the salt with which to flavor their venison. Here, while engaged in procuring this necessary condiment, was he surprised and captured by the Indians; and here was fought one of the most disastrous, to the whites, of the early battles with the savages. The historian of Kentucky will always connect the name of this place with some of the most interesting events of its early annals.

Its history anterior to the advent of the white race—unwritten except on the faces of the sterile hills around the spring, is doubtless equally eventful; for to this spot, in that early period, congregated immense herds of Buffaloes and other wild inminantia; led by mysterious instinct from distant parts of the continent to drink the saline waters; and making in their progress immense roads or trails, through the woods and the dense cane-brake, some of which are to be traced even at the present day. To this cause doubtless—viz: the feeding and trampling of these immense herds over the immediately neighboring hills, destroying the cane and grass, together with the subsequent removal of the forest trees by the pioneer salt boilers, leaving the soil exposed to the washing influence of the rains;—is to be attributed the remarkable appearance of these hills. Denuded of their soil, presenting a surface of broken rocks, and barely shaded by a scanty growth of stunted cedars. A singular region of sterility in the midst of a country of the highest fertility. Doubtless, in later years, these hills may again acquire a soil, by the disintegration of the rock, under the protective agency of vegetation, but they now illustrate the extreme slowness with which it is produced, even from a limestone which is by no means remarkable for its resistance to the atmospherical agencies.

The geological formation in which the Blue Lick Springs are located, is the same as that which underlies Cincinnati and the central fertile region of Kentucky, called by the western geologists the great Blue Limestone formation. It is a lower member of the so-called Silurian System of Murchison. It is a formation of great thickness in the west, composed of limestone layers of greater or less thickness, hardness and purity, with beds of bluish marley clay presenting sometimes a shaley structure; all rich in the fossilized remains of inhabitants of the deep primeval ocean under which they were evidently deposited. These fossils are

---

* See Dr. Yandell on the mineral Springs of Kentucky. Transylvania Journal of Medicine, 1832, vol. 5, page 385

† In late years, the accommodations have been greatly improved at this old watering place, which is now under the management of the Messrs. Holday.

‡ Put up in tight vessels it bears transportation very well; but as it is speedily altered after exposure to the air, it should be bottled, and corked and sealed very perfectly for distant use.

numerous *orthocerata*; *trilobites*, especially the large *Isotelus gigas;* the characteristic coral the *chaetetes lycoperdon;* some *crinoidian* remains; a few *cyathophilla;* with a great variety of shells of mollusca, of the genera *Delthyris, Leptæna, Orthis, Atrypa, Pleurotomaria Bellerophon, &c., &c.* On this Blue Limestone are seated the richest and most durable lands of the west, characterising the region in which this formation comes to the surface. These lands doubtless owe their fertility to this rock—from whence the soil has probably been derived by its slow disintegration,—which abounding in phosphate of lime, the alkalies, and the other mineral elements of the food of plants, especially in those layers which are rich in fossil remains, gives the peculiar fatness to the soil which is formed from it. §

The well known Big Bone Lick of Kentucky is seated on this same rock formation, and the composition of the water of the spring in that locality appears, by all accounts, to be nearly analogous to that of the Blue Licks; it being a saline sulpur spring like the latter. Indeed, the Blue Limestone is very generally known as a saliferous formation; which is doubtless to be referred to its sub-marine origin. Numerous springs of salt water have been found on it, and many salt wells, some containing sulphuretted hydrogen, have been obtained in it by boring.

At the Blue Licks, beside the main spring, there are a number of minor ones, on the two sides of the Licking river and in its bed, the water of some of which has been examined by the author, and found to be very much like that of the principal spring in composition. Johnson's well, in Scott county, Ky., also presents a composition somewhat analogous to that of the Blue Lick water, but it is much weaker and contains more magnesian salts.

While the water of the superficial wells and springs, on this formation, are generally what is denominated *hard* or *limestone water*—containing bi-carbonates of lime and magnesia, with a little iron, and some phosphate of lime, held in solution by carbonic acid; these salt wells, or "licks," so called, contain chlorides of sodium and potassium, chlorides of calcium and magnesium, sulphate and carbonate of lime, &c., and are frequently impregnated, to a greater or less degree, with sulphuretted hydrogen. Saline water of this character, as above intimated, has been frequently obtained on the Blue Limestone formation by boring. For example, in the little town of Keene, in Jessamine county, Ky., a water was obtained in this manner, in 1848, by Mr. Wm. R. Dean, which is a very good salt sulphur water, and has been considerably employed for its medicinal properties. It contains sulphuretted hydrogen and carbonic acid gases; bi-carbonates of lime and magnesia, with a trace of bi-carbonate of soda; chlorides of sodium, calcium, magnesium, and doubtless of potassium, with a trace of iron; but this is much weaker than the Blue Lick water containing only 1 6 grains of saline in the 1000 grains of the water; being only about one sixth the strength of the former. In a later testing, in May, 1850, it was found to be yet weaker, probably because of the then extremely wet season.—This water has not been fully analyzed to detect the presence of iodine and bromine.

In Scott county of this State, in a well bored to the depth of 176 feet in this limestone, Mr. W. Roszell obtained a water which contains a notable proportion of chlorides of sodium, calcium and magnesium, &c., &c., and smells strongly of sulphurretted hydrogen. The water of another bored well—105 feet deep, obtained in 1848 by Major B. Roberts, in Harrison county, also on the Blue Limestone Formation,—has a very slight bituminous or sulphureous odor, but contains as much as sixteen parts in the thousand of saline matters, principally chloride of sodium, with chlorides of potassium, calcium and magnesium; sulphate of lime; bi-carbonates of lime, magnesia and iron, and a trace of iodine. This is rather stronger in salts than the Blue Lick water, and differs from it also in its deficiency of sulphuretted hydrogen, but in other respects they resemble each other very much in composition.

Another well, 81 1-2 feet deep, was made by boring, in Scott county, near Georgetown, on the property of Mr. R. Ford, the water of which contains as much as 4 per cent. of saline matter, principally common salt, with sulphates of lime and potash, chlorides of calcium and magnesium, &c., &c. Some of the wells in Lexington yield a water smelling slightly of sulphuretted hydrogen, and while penning these remarks, a bottle of water was brought to me from a boring in progress, forty-

---

§ In the year 1849 the author submitted two different specimens of the Blue Limestone, from the different layers to chemical analysis, with a view to ascertain its agricultural relationships. The results, as published at the time in the Albany Cultivator, (vol. vi., p. 105, 1849,) are as follows:

	SPECIMEN 1.	SPECIMEN 2.
Carbonic Acid	36,675	40,53
Phosphoric Acid	1,350	36
Sulphuric Acid	807	not estimated.
Lime	47,046	50,97
Magnesia	900	66
Alumina and oxide of Iron	9,880	57
Fine Sand and Silicates	1,790	6,52
Moisture and loss	1,552	49
	100,000	100,000

In addition to these ingredients, potash and soda were obtained from the limestone in notable proportions; as much as 0.0487 per cent of potash, in one case, and 0.0058 per cent in another. It is probable that a considerable proportion of the iron is in the form of carbonate of the protoxide in the recently exposed blue rock, while some little is present as a sulphuret.

five feet deep, in this city, which is a weak sulphur water.**

Saline, and saline sulphur-waters, therefore are quite frequent, comparatively, in our Blue Limestone strata; but amongst all the springs of this nature, known at present on this formation, in Kentucky, none are as valuable, and as remarkable, in many respects, as those of the lower Blue Licks.

The principal spring, of this locality, from which the water submitted to analysis was taken, is situated near the banks of the Licking river, flowing out about twenty feet above low water in that stream. It rises in a hexagonal basin of stone, which has been built for it, which is six feet two inches in diameter from one side to the opposite parallel one, and about five or six feet in depth. The quantity of water which flows out varies in different seasons. When the water for the present examination was obtained, June 6, 1850, it was low in the spring and not running. The water in this basin was lowered about one foot by pumping out seventy-six barrels* in the course of three hours; and in the winter time the stream which flows out from it would probably fill a pipe three inches in diameter.

The temperature of this spring was observed by Major Richard Owen, Professor in the Western Military Institute located at the Blue Licks; who was kind enough also to procure and pack up for me with great care, the water, sediment and gas, from the spring, in the various bottles which had been prepared for the purpose. In six observations, at different times on June 4th and 5th, the external air varying from 60 degs. to 76 degs. Fahr., the temperature of the water stood very constantly at 62 degs. This is about seven degrees above the mean temperature of this region, which is about 55 degs.; and it is probable that the temperature of the water in the basin had been somewhat raised by the external heat of the atmosphere. When flowing rapidly it may perhaps be found to approximate more nearly to the mean annual temperature.

The mass of water in the spring presents a light-yellowish-green color; partly owing, perhaps, to the reflection from the yellowish grey sediment; for when it is taken up in a clear vessel it appears perfectly colorless and beautifully transparent.—On standing exposed to the air, however, it becomes of a yellowish-green color, very perceptible in a white pitcher, or even in a white glass bottle. This color deepens on boiling the water,—but boiling does not cause it to appear in the recent water. This color, to which the spring probably owes its name of *Blue* Licks, is due to the decomposition of some of the dissolved ingredients. On exposure to the air, the hydrogen, of the sulphuretted hydrogen, becomes converted into water by combining with oxygen from the atmosphere, while the sulphur, with the trace of iron, &c., are deposited as a light yellowish-green precipitate; at the same time, in consequence of the escape of some of the free carbonic acid, carbonate of lime is thrown down, which mixes with the sulphur precipitate. The minute portion of iron which exists in the recent water, probably, as carbonate of the protoxide, losing its carbonic acid and oxygen, becomes a sulphuret by taking some of the sulphur of the decomposed sulphuretted hydrogen, and gives the greenish tinge to the water and its sediment.

In the water which has been bottled or brought in barrels from the spring, this change of color and consequent deposition, occurs a few hours after it has been brought in contact with the air by uncorking and withdrawing a portion out of the vessel. It changes in a marked manner in flavor owing to the decomposition of the sulphuretted hydrogen; and after a few days exposure loses almost all smell and taste of this gas; as might be expected from its decomposible nature. To preserve its virtues in exportation, therefore, it should be bottled like a sparkling wine and used as soon as it is opened. In this manner, if but little air be left in the neck of the bottle and the cork is very tight and secured by sealing wax, it may be preserved unchanged for a considerable time. In the spring and its channel this decomposition and escape of gas continually takes place, causing the formation of sediment. Less decomposition would probably take place in the spring were its basin smaller, so that the water would be more rapidly renewed and it would expose less surface to the air.

Some of the *sediment* collected from the bottom of the spring, was found by analysis to contain the following ingredients, viz:

Sand, in considerable proportion.
Carbonates of lime and Magnesia,
Sulphur,
Oxide and sulphuret of Iron,
Alumina,
A trace of oxide of Manganese,
Apocrenic Acid,
A trace of Crenic Acid.

All these ingredients, except the sand, which is probably brought out mechanically suspended, were doubtless dissolved in the recent water, and were deposited on its exposure to the air.

In addition to the gases, sulphuretted hydrogen and carbonic acid, which are thus gradually decomposed in the water, or which escape insensi

** Associated with the water thus obtained by boring, in our Blue Limestone, is sometimes found a large quantity of light carburetted hydrogen gas. One remarkable instance occurred in Franklin county, at the mills of the Messrs. Stedman, where, as I am informed, this gas, in large quantities is poured out from the boring; the stream lasting for some time and perhaps existing at the present moment. The origin of this gas in the coal formations, where it is more abundant, is doubtless from the vegetable matters which formed the coal, but in this formation it is a puzzle to geologists. Unless we suppose it to be derived, like the fluid bitumen sometmes discovered in this rock, from the decomposition of the animal remains in the strata, no other probable cause can be given for its production.

* These barrels will not contain more than thirty gallons.

bly from its surface, streams of bubbles of gas are continually rising through the spring and breaking into the atmosphere.

Some of this gas, carefully collected for me by M j. Owen, in bottles prepared for the purpose, was submitted to analysis, and found to consist mainly of nitrogen, mixed with about 4 5 per cent, of carbonic acid gas, containing only a trace of sulphuretted hydrogen.

The analysis of the water was performed in the chemical laboratory of the Medical Department of Transylvania University, at Lexington, with the assistance of Mr. A. Schue, of the Western Military Institute, and required at least ten days constant labor. I will not give the detail of the various processes, as this would be uninteresting to the general reader. Let it suffice to say that the amount of free sulphuretted hydrogen and carbonic acid was ascertained by placing, by means of proper pipette, a measured quantity of the recent water, at the spring, in bottles containing, severally, solution of arsenious acid in hydrocholoric acid, and an amonical solution of chloride of calcium. The precipitates in these bottles were examined in the laboratory, and the proportion of these gases accurately ascertained.

The estimation of the saline ingredients was made in the most careful manner, in some of the water which had been brought from the spring in tight glass-stoppered bottles. The quantity used in each estimation was not less than one thousand grains, and was sometimes as much as twelve thousand grains.

To estimate the Bromine and Iodine, a demijohn which would hold about one hundred pounds, was sent to the springs to be filled: intending to evaporate this quantity for the purpose; but by some accident it did not come to hand in time, and to avoid delay the estimation of these minute ingredients was made by operating on the residue obtained by evaporating 5 1 2 lbs., Troy, of the water; all that was left, of two gallons, from the other experiments. The Iodine was estimated as Iodide of palladium, and the Bromine, precipitated as Bromide of silver was estimated by the *in direct* method as described in the recent works on chemical analysis.

The proportions of the alkalies were also separately estimated. In consequence of the failure to obtain the carboy of water, the *separate* proportions of the alumina, phosphate of lime, and oxide of proto-carbonate of iron, were not made out; this, however, is a matter of minor importance.*

The composition of the Blue Lick water, according to this analysis, is as follows; calculated both in 1000 grains of the water and in the wine pint of 7,680 grains, v.z:

Specific Gravity,	1 007		
Gases in 1000 grains.		in the wine pint.	
	Cubic inch.	Gr.	Cubic inch.
Sulphuretted hyd. gas, 0,039-7 grs.	0 1086	0.3031129	0 824048
Free Carb. Acid gas. 0.3547 grs.	0.75	2 724096	5.5308

The former is in the proportion of about 1-36.h, the volume of the water and the latter about 1-5.h the volume.

Saline constituents in 1000 grains		in the wine pint.
Carbonate of lime,	3 [illegible] grains	2 [illegible] grains.
Carbonate of magnesia,	20 5 "	[illegible] "
Alumina, phosphate of lime		
and oxide of iron	0 6 3 "	0 0 1.774 "
Chloride of sodium,	8 3 [illegible] "	64.1 2102 "
Chloride of potassium,	[illegible] "	0.1 4 0.7 "
Chloride of magnesium,	0 [illegible] 28 1 "	4 0 [illegible] "
Bromide of magnesium,	0 [illegible] 34 "	0 0 [illegible] 6 "
Iodine of magnesium,	0 0003 40 "	0 0.0.671 "
Sulphate of lime,	0 5.3 [illegible] "	4.2 [illegible] "
Sulphate of potash,	0 5 0 190 "	1 4 [illegible] "
Silicic acid,	0 0 79100 "	0.1377792 "
Loss,	0 2819-61 "	2.1 [illegible] "
Whole saline contents,	10.3000000	79 1040000

The water also contains traces of oxide of manganese, and apocrenic and crenic acids.†

As it respects the medicinal virtues of this water it is not necessary for me to say much — Knowing the nature and proportions of the ingredients, any well educated physicians will understand its medicinal virtues and applications. It is undoubtedly a highly valuable saline sulphur water and consequently acts as a nervous stimulant, diaphoretic diuretic and emmenagogue; proving purgative only to some persons. Such waters are described by authors to be useful in chronic disorders of the liver, dyspepsia, chronic cutaneous diseases, chronic rheumatism and gout, secondary syphilis, dysmenorrhœa, &c., &c.; and this water would doubtless be valuable in some scrofulous afflictions, more especially from the iodine and bromine which it contains.

The discovery of these ingredients in this water is a matter of great interest in a medicinal point of view. Although they exist in i in very small proportions, yet experience has demonstrated that they are in sufficient amount to be act ve when the use of the water is continued for a length of time, in the quantities usually drank at the springs.

The use of the water as a bath is a valuable adjuvant to its internal use in many cases. Its application to the cure of disease should, however, always be made under the directions of a physic an.

---

† The quantity of saline and other matters brought out from the interior by this and other similar springs is immense, and sets at defiance all efforts to find out their source.

Taking the data above given as to the quantity of water which flows out at this spring, we find that it emits 678 gallons per hour, equal to 26,272 gallons in the day of twenty-four hours. Supposing the saline matters to constitute but one per cent. of the water, the amount brought out in one hour would be more than 58 lbs. avoirdupois. But say that 50 lbs. an hour is the proportion, and the quantity will amoun to 438,000 lbs. per annum. The specific gravity of common salt being 2.257, this quantity in solid lump would contain about 310 cubic feet, or be enough to form a cube of salt nearly 7 feet on a side! And yet the water flows on without any sensible dimunition of its saltness. Whence is all this saline matter obtained? Is there embedded in the deeper strata of the Blue limestone, an immense layer of rock salt, derived from the original ocean under which the rock was deposited?